

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-226436

(43)Date of publication of application : 21.08.2001

(51)Int.Cl. C08F216/14
 C08F214/18
 C08F293/00

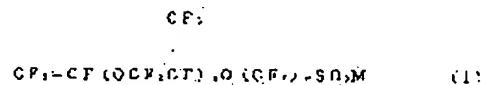
(21)Application number : 2000-038704 (71)Applicant : DAIKIN IND LTD
 (22)Date of filing : 16.02.2000 (72)Inventor : TATEMOTO MASANAGA

(54) METHOD FOR PRODUCING FLUORINE-BASED IONOMER COPOLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a sulfonic group-containing fluorine-based ionomer copolymer in a state of being readily purified.

SOLUTION: This method for producing a fluorine-based ionomer copolymer is characterized in that (i) a compound of the following formula (1) [M is an alkali metal or an alkaline earth metal; m is an integer of 1 to 4; n is 0, 1 or 2] is copolymerized with (ii) tetrafluoroethylene and (iii) at least one kind selected from the group consisting of hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, perfluoroalkyl vinyl ether ($CF_2=CFOCF_2CF_2CF_3$) and ethylene as a third monomer in the presence of a polymerization initiator.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

[Claim(s)]

[Claim 1] (i) The following type (1)

[Formula 1]

CF,

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CF₂=CF (OCF₂CF) .O (CF₂) .SO₂M (1)

M shows alkali metal or alkaline earth metal among [type. m shows the integer of 1-4 and n shows 0, 1, or 2.] The manufacturing method of the fluorine system ionomer copolymer characterized by copolymerizing at least one sort chosen from the group which comes out and serves as a compound expressed and (ii) tetrafluoroethylene from hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, perfluoroalkyl vinyl ether (CF₂=CFORf (Rf shows the perfluoroalkyl radical of carbon numbers 1-5)), and ethylene as the third (iii) monomer under existence of a polymerization initiator.

[Claim 2] (i) The following type (1)

[Formula 2]

CF,

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CF₂=CF (OCF₂CF) .O (CF₂) .SO₂M (1)

M shows alkali metal or alkaline earth metal among [type. m shows the integer of 1-4 and n shows 0, 1, or 2.] Come out and as the third (iii) monomer with the compound expressed and (ii) tetrafluoroethylene Hexafluoropropylene, Chlorotrifluoroethylene, vinylidene fluoride, perfluoroalkyl vinyl ether (CF₂=CFORf (Rf shows the perfluoroalkyl radical of carbon numbers 1-5)) And at least one sort chosen from the group which consists of ethylene is copolymerized under existence of a polymerization initiator and an iodine system compound.) — Process: and the fluorine-containing polymer chain segment B and tetrafluoroethylene which form the fluorine-containing polymer chain segment B containing a sulfuric group. They are hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, and perfluoroalkyl vinyl ether (CF₂=CFORf (Rf shows the perfluoroalkyl radical of carbon numbers 1-5)) as the third monomer.) — and the manufacturing method of the fluorine system ionomer block copolymer which at least one sort chosen from the group which consists of ethylene is made to react to the bottom of existence of a polymerization initiator, and includes the process which forms a different fluorine-containing polymer chain segment A from the fluorine-containing polymer chain segment B.

[Claim 3] The manufacturing method according to claim 1 or 2 whose third monomer is hexafluoropropylene and/or perfluoroalkyl vinyl ether (CF₂=CFORf (Rf shows the perfluoroalkyl radical of carbon numbers 1-5)).

[Claim 4] How to remove the quality of a low-molecular-weight toxicity impurity while collecting the unreacted objects of the compound expressed with the following formula (1) an ultrafiltration or by dialyzing in the solution or dispersion liquid of the fluorine system ionomer copolymer

obtained according to the manufacturing method according to claim 1 or 2, or a fluorine system ionomer block copolymer.

[Formula 3]

CF,

|

CF₂=CF (OCF₂CF) .O (CF₂) .SO₂M (1)

M shows alkali metal or alkaline earth metal among [type. m shows the integer of 1-4 and n shows 0, 1, or 2.]

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of the fluorine system ionomer copolymer containing a sulfonic group.

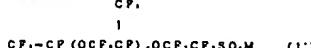
[0002]

[Description of the Prior Art] As a fluorine system ionomer, the copolymer which combined the sulfonic group thru/with the carboxyl group with fluorination polymer chains, such as Nafion (trademark) and deflection myon (trademark), is known. These are developed as ion exchange membrane mainly used for battery electrolysis, a chemical sensor, a demarcation membrane, and a macromolecule super-strong acid catalyst are begun, and the utilization as a proton transport polyelectrolyte of a fuel cell etc. is considered.

[0003] As this fluorine system ionomer, it is the following type (1') to WO 98/No. 43952 pamphlet.

[0004]

[Formula 4]



[0005] M shows alkali metal or alkaline earth metal among [type. n shows 0, 1, or 2.] It comes out and the copolymer of the monomer (it abbreviates to "S monomer" hereafter) expressed and other monomers is indicated.

[0006] However, the aquosity dispersion of the copolymer obtained when other monomers are tetrafluoroethylenes was especially unstable when there were comparatively few especially S monomers, and when it compounded to a large quantity, purification of the obtained copolymer was not easy.

[0007]

[Problem(s) to be Solved by the Invention] This invention offers easily the manufacturing method of the fluorine system ionomer copolymer which can be refined.

[0008]

[Means for Solving the Problem] It found out that this invention person's stability of the aquosity dispersion of the copolymer obtained by carrying out copolymerization of the third monomer in addition to S monomer and tetrafluoroethylene of a general formula (1) improves as a result of repeating examination in view of the above-mentioned technical problem, and the obtained 3 yuan or more copolymer removed quality of a low-molecular-weight ionicity impurity, such as a residual monomer, easily by the ultrafiltration method, dialysis, etc., and could be refined.

[0009] This invention relates to the following term 1 - a term 3.

Term 1. The (i) following type (1)

[0010]

[Formula 5]

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CF₃

I



[0011] M shows alkali metal or alkaline earth metal among [type. m shows the integer of 1-4 and n shows 0, 1, or 2.] The manufacturing method of the fluorine system ionomer copolymer characterized by copolymerizing at least one sort chosen from the group which comes out and serves as a compound expressed and (ii) tetrafluoroethylene from hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, perfluorosulfonyl vinyl ether (CF₂-CFORf (RF shows the perfluoralkyl radical of carbon numbers 1-5)), and ethylene as the third (iii) monomer under existence of a polymerization initiator.

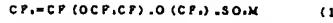
Term 2. The (i) following type (1)

[0012]

[Formula 6]

CF₃

I



[0013] M shows alkali metal or alkaline earth metal among [type. m shows the integer of 1-4 and n shows 0, 1, or 2.] Come out and as the third (iii) monomer with the compound expressed and (ii) tetrafluoroethylene Hexafluoropropylene, Chlorotrifluoroethylene, vinylidene fluoride, perfluorosulfonyl vinyl ether (CF₂-CFORf (RF shows the perfluoralkyl radical of carbon numbers 1-5.) And at least one sort chosen from the group which consists of ethylene is copolymerized under existence of a polymerization initiator and an iodine system compound) — Process; and the fluorine-containing polymer chain segment B and tetrafluoroethylene which form the fluorine-containing polymer chain segment B containing a sulfonic group. They are hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, and perfluorosulfonyl vinyl ether (CF₂-CFORf (RF shows the perfluoralkyl radical of carbon numbers 1-5.)) as the third monomer, — and the manufacturing method of the fluorine system ionomer block copolymer which at least one sort chosen from the group which consists of ethylene is made to react to the bottom of existence of a polymerization initiator, and includes the process which forms a different fluorine-containing polymer chain segment A from the fluorine-containing polymer chain segment B.

Term 3. The term 1 whose third monomer is hexafluoropropylene and/or perfluorosulfonyl vinyl ether (CF₂-CFORf (RF shows the perfluoralkyl radical of carbon numbers 1-5.)) or manufacturing method given in 2.

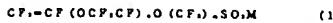
Term 4. How to remove the quality of a low-molecular-weight ionicity impurity while collecting the unreacted objects of the compound expressed with the following formula (1) to a term 1 or 2 an ultrafiltration or by dialyzing in the solution or dispersion liquid of the fluorine system ionomer copolymer obtained according to the manufacturing method of a publication, or a fluorine system ionomer block copolymer.

[0014]

[Formula 7]

CF₃

I



[0015] M shows alkali metal or alkaline earth metal among [type. m shows the integer of 1-4 and n shows 0, 1, or 2.]

[0016]

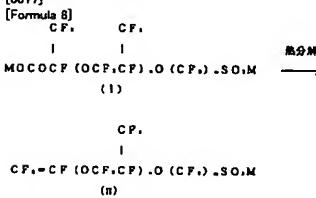
[Embodiment of the Invention] The raw material compound expressed with the general formula (1) used by the approach of this invention is well-known, for example, can be manufactured by the approach of a publication in WO 98/No. 43952 pamphlet. That is, according to the following

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scheme, it can manufacture by the pyrolysis of a corresponding raw material.

[0017]



[0018] M shows alkali metal or alkaline earth metal among [type. m shows the integer of 1-4 and n shows 0, 1, or 2.] S monomer expressed with a general formula (1) in the copolymer of this invention, tetrafluoroethylene (TFE), and the hexafluoropropylene as the third monomer. Chlorotrifluoroethylene, vinylidene fluoride, perfluorosulfonyl vinyl ether (CF₂-CFORf (RF shows the perfluoralkyl radical of carbon numbers 1-5.)) — and at least one sort of ratios chosen from the group which consists of ethylene — S monomer:TFE — the third — it is monomer 5-49 mol % 49 mol 9.4-50 mol 9.5 - 20 mol %. Here, in order to stabilize the polymer solution or polymer dispersion liquid to generate, as for the third monomer, it is desirable to use a necessary minimum amount to TFE.

[0019] In the manufacturing method of this invention, under existence of the source of radical initiation, it copolymerizes easily, and can manufacture, and a fluorine system ionomer block copolymer can also be manufactured by copolymerizing under existence of an iodine system compound. The iodine migration polymerization method using this iodine system compound itself is well-known (for example, refer to macromolecule collected-works 765-783 pages of the 10 volume [49th] No. (1992)).

[0020] As an iodine system compound to be used, for example 1,3-diodo perfluoro propane, 1,4-diodoperfluorobutane, 1, 3-diodo-2-chloro perfluoro propane, 1, 5-diodo-2, 4-dichloro perfluoro pentane, 1, 8-diodo perfluoro hexane, Perfluoro ARUKI range iodide, such as 1, 8-diodo perfluoro octane, 1, 12-diodo perfluoro dodecane and 1, and 18-diodo perfluoro hexadecane. Perfluoro alkyl iodide and diiodomethane, 1, and 2-diodo ethane is mentioned. [which have unsaturated bonds, such as CF₂-CFI and CF₂-CFOCF₂CF2I,] These compounds may be used independently, and can also be combined and used mutually, 1,4-diodoperfluorobutane is desirable especially. Jo — base — the amount of a compound is 0.01 - 1 % of the weight to the sum total weight of each monomer.

[0021] The polymerization initiator used by the manufacturing method of this invention may be the same as what is used for the polymerization of a fluorine system polymer from the former. There is an azo compound in these initiators at an organic and inorganic peroxide list. As a typical initiator, there are persulfate, peroxidation carbonate, and peroxidation ester and ammonium persulfate (APS) is mentioned as a desirable initiator. APS may be used independently and can also be used combining a reducing agent like ascorbic acid, sulfites, and perfluoro alkyl sulfonic acid salts. The amount of a polymerization initiator is 0.01 - 1 % of the weight to the sum total weight of each monomer.

[0022] When manufacturing a block copolymer, it is carried out at least two steps of reactions.

[0023] The manufacturing method of a block copolymer is explained taking the case of one phase of the following example 1 - 4 phase.

[0024] It is thought that dispersion generates one phase of an example by the micelle-like solution (or sol) which consists of a polymer minute particle which combined iodine with the

polymer chain and with the low molecular weight which is the phase of preparing seed (seed) of the copolymer manufactured by this invention, and becomes I-A-I according to this phase, and the case. The minute particle generated here moves to the two to 3 next phase. This two phase ~ 3 phase prepares polymer chain segment-B which contained as many S monomers as possible fundamentally, although the charges of S monomer differ for a while. The polymer to generate serves as I-B-A-B-I. It is effective in not decelerating the place where a polymerization reaction rate originally becomes slow at the process of two phase - 3 phase (process which increases the molecular weight of the -B-part of I-B-A-B-I, and S monomer content of the whole polymer at the process that this is the same) by making the minute particle of many in the phase of I-A-I as possible. In this way, after making the molecular weight of the whole polymer molecule (I-B-A-B-I) increase, it goes into four phase. Once dilute in this phase 3 times, and reduce the concentration of S monomer and it is set up to the same extent as one phase. 1) Polymer chain segment-A' which can crystallize the water-insoluble nature of a presentation comparable as a phase can be made to be able to form, and it can consider as the block copolymer of the form of I-A'-B-A-B-I as a result. 1) Although gradual-A' has also set up the almost same presentation as A'-, since molecular weight is small, it may become water solubility by the case.

[0025] Generally, the molecular weight of the polymer chain segment A is about 5000-1 million, and may be adjusted by the ratio of polymer **** and an iodine system compound charge. moreover, the weight ratio of the polymer chain segment B and polymer chain segment A'A' - (9.2) (5.9) — it can choose freely [it is desirable and] in the range of - (9.65) (40.80). The molecular weight of the whole block copolymer is about 5000 - abbreviation 3 million.

[0026] The obtained copolymer or block copolymer is obtained as stable aquosity dispersion, and can remove easily unreacted objects, such as S monomer which is a raw material, and the quality of an ionicity impurity of low molecular weight (for example, a polymerization initiator and its decomposition product) with an ultrafiltration etc.

[0027] The copolymer of this invention may be two or more block copolymers or graft copolymer which could copolymerize at least one sort by the fixed ratio of S monomer, tetrafluoroethylene, and the third monomer of the above, and connected the segment with the high ratio of S monomer, and the segment which carried out sequential reduction of the ratio of S monomer. A graft copolymer can be obtained when CF₂-CFOCF₂CF2I etc. is adopted as an iodine system compound.

[0028] The ionomer manufactured by the approach of this invention can give the advantageous and unique engine performance on the occasion of the utilization to the fuel cell which used ion exchange membrane, such as selective ion permeability and stereospecificity, a sensor, permselective membrane, a catalyst, a solid electrolyte, and it.

[0029]

[Effect of the Invention] According to this invention, the fluorine system ionomer copolymer containing a sulfonic group useful as a strong acid nature fluorine system polyelectrolyte can be easily obtained in the condition which can be refined. Especially a fluorine system ionomer block copolymer has the effectiveness of restraining the whole polymer molecule also containing the fluorine-containing polymer chain segment which contains a sulfonic group as a result by crystallinity by the crystal part, and increasing the mechanical strength of a plastic solid.

[0030]

[Example] Hereafter, this invention is explained more to a detail using an example and the example of a comparison.

CF₂-CFOCF₂CF2I 300g 3Cl which was newly refined by rectification] 1 and jig lime 4g which dehydrated are put into the 11. flask which attached the example of reference 1 stirring aerofoil, the thermometer, the nitrogen gas (N₂) inlet, and the reflux cooling pipe. It was careful of NaOOCCH₂CF₃ OCF₂CF₂SO₃Na which carried out heating dehydration at 130 degrees C as powdered for 2 hours not to absorb moisture, and taught quickly the bottom of stirring, introducing desiccation N₂ gas by part for 50ml/l, and heating was promptly started with the mantle heater. Reflux began in the place which amounted to 200 degrees C after 20 minutes, and it was admitted that the capacity emitted to a pan from a reflux cooling pipe top after 5 minutes

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increased rapidly. About about 20 minutes, after continuing a reaction, the switch of a mantle heater was turned off in the place where generating of gas is no longer seen mostly, and the flask was quenched to the room temperature for 5 minutes in the ice-cooling bath. Reaction temperature was a maximum of 207 degrees C. [0031] The brown granular powder distributed in $C_6CF_2CFC_1$ 3Cl was filtered with the glass, filter, and the granular powder which was air-dried and was colored a little after washing by little HFCFC225 was acquired. Next, this granular powder was dissolved in 200ml of pure water, after adjusting to pH=7 was again taken the ** exception in the NaOH water solution 10%, and filtrate was passed. The white residue on a filter was NaF. When filtrate was covered over the evaporator, moisture was evaporated and the whole solidified by the damp or wet condition mostly, it once moved on the glass filter after 1-hour heat insulation in the 5-degree C refrigerator, and filtration-under-reduced-pressure processing was carried out in about 2-hour room temperature atmospheric air. On evaporation and a filter, white crystalline powder remained [the brown liquid] gradually, $CF_2=CFOC_2CF_2SO_3Na$ (S monomer) which ***** the obtained white crystalline powder from water, and is made into the object was obtained.

Example 11 To the proof-pressure reaction vessel made from stainless steel of 5L equipped with a thermometer distance pipe and gas installation tubing, pure water 2L, 0.1g (APS) of ammonium persulfate, S monomer obtained in the example 1 of reference 60g, 1,4-diiodoperfluorobutane 0.6g is put in. Under stirring a building envelope by the repeat of fine application of pressure / vacuum by hexafluoropropylene (HFP) After a permutation, After pressurizing application of pressure and a degree to 1MPa by tetrafluoroethylene (TFE) to 0.3MPa(s) by hexafluoropropylene gas, temperature up was carried out to 60 degrees C. Since pressure drawdown started immediately after the pressure reached 1.15MPa(s) after 30 minutes, pressure was lowered the temperature and discharged to 20 degrees C or less after the failure of pressure of 0.1MPa, and the polymerization reaction was once suspended. A product is transparency dispersion-like, this paragraph story aims at mainly obtaining the nucleus of stable dispersion by the so-called "seed polymerization".

2) It is S monomer to the dispersion generated by 1. 80g and APS 0.05g were added and the polymerization reaction was started by the same actuation as one after adjusting pH to 7.5. Since pressure drawdown started promptly after temperature up at 60 degrees C, when the polymerization was suspended in the place which had the failure of pressure of 0.16MPa(s) 8 hours after, transparent and colorless dispersion was obtained like 1.

3) Follow 2 and it is S monomer 50g and APS 0.1g were added, the same polymerization actuation as 2 was repeated twice, after 18 hours, the polymerization was ended and transparent and colorless dispersion 2160g was obtained. When it fully dried, dissolution recovery of the unreacted S monomer was carried out with the acetone after this and polymer ***** and S monomer content in a polymer were computed by the material balance after evaporating moisture from that part since it did not coagulate even if this dispersion was dramatically stable and it added electrolytic solutions, such as a hydrochloric acid and a potash alum solution, it was 157g and 25.7-mol % respectively.

4) When diluted dispersion 330g of 3 with pure water 3 times, added APS 0.1g, and it taught the same reaction vessel as 1-3, and 0.45MPa was pressurized for space after the permutation by HFP gas by the same actuation, pressure up was further carried out to 0.9MPa(s) by TFE gas and temperature up was carried out to 80 degrees C, pressure drawdown started promptly. Pressure was lowered the temperature and discharged into 20 degrees C in the place which had the pressure drawdown of 0.06MPa(s) 4 hours after, and the polymerization reaction was ended. The product was the transparent dispersion which became cloudy a little.

[0032] A result to polymer ***** which carried out evaporation to dryness of a part of this dispersion, extracted with the acetone, and collected S monomer was 81g, and S monomer content in a polymer was 7.8-mol %. This polymer is considered to be a block copolymer. The result of drawing 1 and parallel thermogravimetric analysis (DTGA) is shown for ^{19}F -NMR of the obtained dispersion in drawing 2. It became clear that the dispersion of the thermal stability of the polymer of this invention whose functional group ^{19}F -NMR spectrum is obtained and is an SO_3Na mold is also good.

The copolymer of TFE and S monomer can be obtained like an example 1 except not using example of comparison 1HFP as a comonomer. The 2 yuan system copolymer obtained has unstable generation dispersion, and the coagulation of a copolymer tends to happen by the polymerization reaction of long duration. Moreover, since the dispersion of this 2 yuan system copolymer is unstable, sedimentation of a copolymer tends to take place in the process refined by the ultrafiltration method or dialysis, and clearance of unreacted S monomer by the ultrafiltration method or dialysis and concentration are difficult for it. Since the dispersion generated in each phase of 1-4 of example 2 example 1 is very stable, it can collect unreacted residual S monomers by application of an ultrafiltration method. If the dispersion generated by 3 and 4 of an example 1 in the cel of Centriprep (trademark) of Amicon is put in and it processes under the centrifugal separation conditions of room temperature 1500G, only S monomer will penetrate ultrafiltration membrane. Furthermore, after adding dispersion to the cel and repeating it several times, when the law was continued adding pure water to a degree, S monomer was removed nearly thoroughly and was able to obtain the concentration dispersion whose polymer concentration is 80%.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] ^{19}F -NMR of the dispersion obtained in the example 1 is shown.

[Drawing 2] The result of the parallax thermogravimetric analysis (DTGA) of the dispersion obtained in the example 1 is shown.

[Translation done.]

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2001-226436

(P2001-226436A)

(43)公開日 平成13年8月21日 (2001.8.21)

(51)Int.Cl.⁷

C 08 F 216/14
214/18
293/00

識別記号

F I

C 08 F 216/14
214/18
293/00

テマコード*(参考)

4 J 0 2 6
4 J 1 0 0

審査請求 未請求 請求項の数4 OL (全7頁)

(21)出願番号

特願2000-38704(P2000-38704)

(22)出願日

平成12年2月16日 (2000.2.16)

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最終頁に続く

(54)【発明の名称】 フッ素系アイオノマー共重合体の製造法

(57)【要約】

【課題】スルホン酸基を含有するフッ素系アイオノマー
共重合体を容易に精製できる状態を得る。

*

C F ,

|

C F , = C F (O C F , C F) , O (C F ,) , S O , M (1)

〔式中、Mはアルカリ金属又はアルカリ土類金属を示す。mは1~4の整数を、nは0、1又は2を示す。〕
で表される化合物と、(ii)テトラフルオロエチレンと、
(iii)第三モノマーとしてヘキサフルオロブロピレン、
クロロトリフルオロエチレン、ビニリデンフルオライ

* 【解決手段】(i)下記式(1)
【化1】
ド、バーフルオロアルキルビニルエーテル(CF₂=CFOCF₂C
F₂CF₃)及びエチレンからなる群から選ばれる少なくとも
1種を重合開始剤の存在下に共重合することを特徴とする
フッ素系アイオノマー共重合体の製造法。

1

2

【特許請求の範囲】

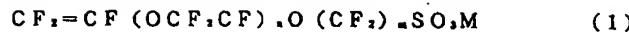
【請求項1】(i)下記式(1)

*【化1】

*

CF₂

|



〔式中、Mはアルカリ金属又はアルカリ土類金属を示す。mは1～4の整数を、nは0、1又は2を示す。〕で表される化合物と、(ii)テトラフルオロエチレンと、(iii)第三モノマーとしてヘキサフルオロプロピレン、クロロトリフルオロエチレン、ビニリデンフルオライド、バーフルオロアルキルビニルエーテル(CF₂=CFORf

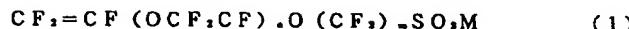
※(Rfは炭素数1～5のバーフルオロアルキル基を示す。)及びエチレンからなる群から選ばれる少なくとも1種を重合開始剤の存在下に共重合することを特徴とするフッ素系アイオノマー共重合体の製造法。

【請求項2】(i)下記式(1)

【化2】

CF₂

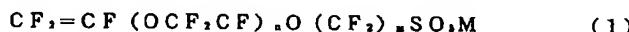
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〔式中、Mはアルカリ金属又はアルカリ土類金属を示す。mは1～4の整数を、nは0、1又は2を示す。〕で表される化合物と、(ii)テトラフルオロエチレンと、(iii)第三モノマーとしてヘキサフルオロプロピレン、クロロトリフルオロエチレン、ビニリデンフルオライド、バーフルオロアルキルビニルエーテル(CF₂=CFORf(Rfは炭素数1～5のバーフルオロアルキル基を示す。)及びエチレンからなる群から選ばれる少なくとも1種を重合開始剤及びヨウ素系化合物の存在下に共重合して、スルホン酸基を含有する含フッ素ポリマー鎖セグメントBを形成する工程；及び含フッ素ポリマー鎖セグメントBとテトラフルオロエチレンと、第三モノマーとしてヘキサフルオロプロピレン、クロロトリフルオロエチレン、ビニリデンフルオライド、バーフルオロアルキルビニルエーテル(CF₂=CFORf(Rfは炭素数1～5のバーフルオロアルキル基を示す。)及びエチレンからな★

CF₂

|



〔式中、Mはアルカリ金属又はアルカリ土類金属を示す。mは1～4の整数を、nは0、1又は2を示す。〕

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、スルホン酸基を含有するフッ素系アイオノマー共重合体の製造法に関する。

【0002】

【従来の技術】フッ素系アイオノマーとしては、ナフィオン(商標)、フレミオン(商標)などの過フッ素化ポ☆

★る群から選ばれる少なくとも1種を重合開始剤の存在下に反応させ、含フッ素ポリマー鎖セグメントBと異なる含フッ素ポリマー鎖セグメントAを形成する工程を含む、フッ素系アイオノマーブロック共重合体の製造法。

【請求項3】第三モノマーがヘキサフルオロプロピレン及び/又はバーフルオロアルキルビニルエーテル(CF₂=CFORf(Rfは炭素数1～5のバーフルオロアルキル基を示す。)である請求項1又は2に記載の製造法。

【請求項4】請求項1又は2に記載の製造法により得られたフッ素系アイオノマー共重合体又はフッ素系アイオノマーブロック共重合体の溶液又は分散液を限外過濾又は透析することにより、下記式(1)で表される化合物の未反応物を回収するとともに低分子量イオン性不純物質を除去する方法。

【化3】

30

CF₂

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☆リマー鎖にスルホン酸基ないしカルボキシル基を結合した共重合体が知られている。これらは主として食塩電解に利用されるイオン交換膜として開発され、化学センサ

40 一、分離膜、高分子超強酸触媒をはじめ、燃料電池のプロトン輸送高分子電解質などとしての利用が検討されている。

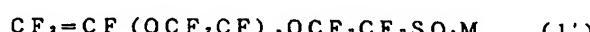
【0003】このフッ素系アイオノマーとしては、WO 98/43952号パンフレットに下記式(1')

【0004】

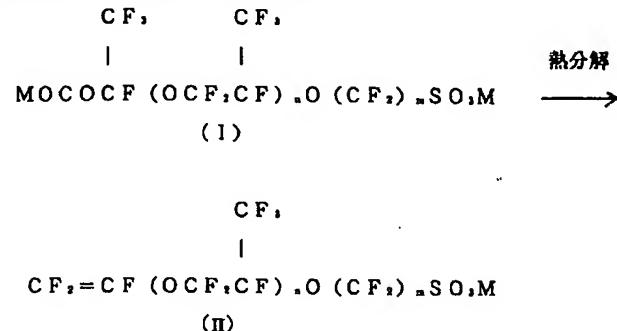
【化4】

CF₂

|



【発明の実施の形態】本発明の方法で用いられる一般式(1)で表される原料化合物は公知であり、例えばWO98/43952号パンフレットに記載の方法により製造できる。すなわち、下記のスキームに従い、対応する*



【0018】(式中、Mはアルカリ金属又はアルカリ土類金属を示す。mは1~4の整数を、nは0、1又は2を示す。)

本発明の共重合体において、一般式(1)で表されるSモノマー、テトラフルオロエチレン(TFE)及び第三モノマーとしてのヘキサフルオロプロピレン、クロロトリフルオロエチレン、ビニリデンフルオライド、バーフルオロアルキルビニルエーテル($\text{CF}_2=\text{CFORf}$ (Rfは炭素数1~5のバーフルオロアルキル基を示す。))及びエチレンからなる群から選ばれる少なくとも1種の比率は、Sモノマー: TFE: 第三モノマー = 5~49モル%: 94~50モル%: 0.5~20モル%である。ここで、第三モノマーは生成するポリマー溶液又はポリマー分散液を安定化するためにTFEに対して必要最小限の量を使用するのが好ましい。

【0019】本発明の製造法においては、ラジカル開始源の存在下に容易に共重合して製造することができ、ヨウ素系化合物の存在下に共重合することにより、フッ素系アイオノマーブロック共重合体をも製造することができる。このヨウ素系化合物を用いるヨウ素移動重合法自体は公知である(例えば、高分子論文集 第49巻第10号(1992)765~783頁参照)。

【0020】用いるヨウ素系化合物としては、例えば1,3-ジヨードバーフルオロプロパン、1,4-ジヨードバーフルオロブタン、1,3-ジヨード-2-クロロバーフルオロプロパン、1,5-ジヨード-2,4-ジクロロバーフルオロベンタン、1,6-ジヨードバーフルオロヘキサン、1,8-ジヨードバーフルオロオクタン、1,12-ジヨードバーフルオロデカンおよび1,16-ジヨードバーフルオロヘキサデカンなどのバーフルオロアルキレンジアイオダイド、 $\text{C F}_2=\text{C F I}$ や $\text{C F}_2=\text{CFOCF}_2\text{CF}_2\text{I}$ などの不飽和結合を有するバーフルオロアルケニルアイオダイド、ジヨードメタン、1,2-ジヨードエタンが挙げられる。これらの化合物は単独で使用してもよく、相互に組み合わせて使用

* 原料の熱分解により製造できる。

【0017】

【化8】

することもできる。なかでも1,4-ジヨードバーフルオロブタンが好ましい。ヨウ素化合物の量は、各モノマーの合計重量に対して0.01~1重量%である。

【0021】本発明の製造法で使用する重合開始剤は、20 従来からフッ素系ポリマーの重合に使用されているものと同じものであってよい。これらの開始剤には有機及び無機の過酸化物並びにアゾ化合物がある。代表的な開始剤として、過硫酸塩類、過酸化カーボネート類、過酸化エステル類などがあり、好ましい開始剤として過硫酸アンモニウム(APS)が挙げられる。APSは単独で使用してもよく、またサルファイト類、亜硫酸塩類、バーフルオロアルキルスルフィン酸塩類のような還元剤と組み合わせて使用することもできる。重合開始剤の量は、各モノマーの合計重量に対して0.01~1重量%である。

【0022】ブロック共重合体を製造する場合には、少なくとも2段階の反応で行われる。

【0023】ブロック共重合体の製造法を、下記の実施例1の1)段階~4)段階を例に取り説明する。

【0024】実施例の1)段階は、本発明で製造される共重合体のシード(種)を調製する段階で、この段階によりI-A-Iなる低分子量でポリマー鎖末端にヨウ素を結合したポリマー微小粒子よりなるミセル状溶液(ないしゾル)、場合によりディスパージョンが生成すると40 考えられる。ここで発生する微小粒子が次の2)~3)段階へ移る。この2)段階~3)段階は、Sモノマーの仕込量が少し異なるが基本的にはSモノマーをできるだけ多く含有したポリマー鎖セグメント-B-を調製する。生成するポリマーはI-B-A-B-Iとなる。I-A-Iの段階でできるだけ多くの微小粒子を作つておくことにより2)段階~3)段階(これは同じ工程でI-B-A-B-Iの-B-部分の分子量とポリマー全体のSモノマー含有量を増加していく過程)の工程で重合反応速度が本来遅くなるところを減速させないでむ効果がある。こうしてポリマー分子(I-B-A-B-I)

1) 全体の分子量を増加させてから4)段階に入り、この段階でいったん3倍に希釈してSモノマーの濃度を低下させ、1)段階と同程度に設定し、1)段階と同程度の組成の水不溶性の結晶化可能なポリマー鎖セグメント-A'-を形成させて、結果としてI-A'-B-A-B-A'-Iの形のブロック共重合体とすることができる。1)段階の-A'-とほぼ同じ組成を設定しているが、分子量が小さいため、場合により水溶性となることもある。

【0025】一般にポリマー鎖セグメントAの分子量は約5000～100万であり、ポリマー得量とヨウ素系化合物仕込量の比により調節され得る。また、ポリマー鎖セグメントBとポリマー鎖セグメントA+A'の重量比は、(98:2)～(5:95)、好ましくは(95:5)～(40:60)の範囲で自由に選択できる。ブロック共重合体全体の分子量は、約5000～約300万である。

【0026】得られた共重合体またはブロック共重合体は、安定な水性ディスパージョンとして得られ、原料であるSモノマー等の未反応物、及び低分子量のイオン性不純物質(たとえば、重合開始剤やその分解物)を限外濾過等により容易に除去することができる。

【0027】本発明の共重合体は、Sモノマーとテトラフルオロエチレンと上記第三モノマーの少なくとも1種を一定の比率で共重合してもよく、Sモノマーの比率の高いセグメントと、Sモノマーの比率を順次低減したセグメントを連結した2以上のブロック共重合体又はグラフト共重合体であってもよい。グラフト共重合体はヨウ素系化合物としてCF₃=CFCF₂CF₃、Iなどを採用した場合に得ることができる。

【0028】本発明の方法により製造されるアイオノマーは、例えば選択的イオン透過性、立体特異性などのイオン交換膜、センサー、選択透過膜、触媒、固体電解質やそれを用いた燃料電池などへの利用に際して有利で特異な性能を与える。

【0029】

【発明の効果】本発明によれば、強酸性フッ素系高分子電解質として有用なスルホン酸基を含有するフッ素系アイオノマー共重合体を容易に精製可能な状態で得ることができる。特にフッ素系アイオノマーブロック共重合体は、結晶性で結果的にスルホン酸基を含有する含フッ素ポリマー鎖セグメントをも含むポリマー分子全体を、その結晶部分により拘束して成形体の機械的強度を増大するという効果を有する。

【0030】

【実施例】以下、本発明を実施例及び比較例を用いてより詳細に説明する。

参考例1

攪拌翼、温度計、窒素ガス(N₂ガス)導入口、還流冷却管を付した1リットルのフラスコに300gの新しく

精留により精製したC1(CF₂CFC₁)₃Clと脱水したジグライム4gを入れ、乾燥N₂ガスを50ml/分で導入しながら攪拌下に、粉末状として130°Cで2時間加熱脱水したNaOCOCF(CF₃)OCF₂CF₂SO₃Na 240gを湿気を吸収しないよう注意して素早く仕込み、直ちにマントルヒーターで加熱を開始した。20分後に200°Cに達したところで還流が開始し、さらに5分後に還流冷却管上より放出されるガス量が急激に増加するのを認めた。約20分程度反応を繼續後、ガスの発生がほぼ見られなくなったところでマントルヒーターのスイッチを切り、氷冷浴中で5分間フラスコを室温まで急冷した。反応温度は最高で207°Cであった。

【0031】C1(CF₂CFC₁)₃Cl中に分散した褐色粒状粉末をガラスフィルターで濾過し、少量のHCFC225で洗浄後、風乾して若干着色した粒状粉末を収得した。次に、該粒状粉末を純水200mlに溶解し、10%NaOH水溶液でpH=7に調整後、再度濾別して濾液を採取した。フィルター上の白色残渣はNaFであった。濾液をエバボレーターにかけ、水分を蒸発して全体がほぼ湿润状態で固化した時点で、いったん5°Cの冷蔵庫で1時間保冷後、ガラスフィルター上に移し、約2時間室温大気中で減圧濾過処理した。徐々に褐色の液体がしみ出し、フィルター上には白色結晶性粉末が残存した。得られた白色結晶性粉末を水から再結晶して目的とするCF₂=CFOCF₂CF₂SO₃Na(Sモノマー)を得た。

実施例1

1) 温度計、ガス導入管を備えた5Lのステンレス製耐圧反応槽に純水2L、過硫酸アンモニウム(APS)0.1g、

参考例1で得たSモノマー 60g、1,4-ジヨードバーフル

30 オロブタン0.6gを入れ、攪拌下に内部空間をヘキサフルオロプロピレン(HFP)で微加圧/真空の繰り返しにより置換後、ヘキサフルオロプロピレンガスにより0.3MPaまで加圧、次にテトラフルオロエチレン(TFE)で1MPaまで加圧した後、60°Cまで昇温した。30分後に圧力は1.15MPaに達した後、直ぐに圧力低下が始まるので、0.1MPaの圧力低下の後20°C以下まで降温し、放圧していったん重合反応を停止した。生成物は透明ディスパージョン状である。本段階はいわゆる“種重合”で主として安定なディスパージョンの核を得ることを目的としている。

40 2) 1)で生成したディスパージョンにSモノマー 80g、APS 0.05gを添加し、pHを7.5に調整後、1)と同じ操作で重合反応を開始した。60°Cに昇温後直ちに圧力低下が始まるので、8時間後に0.16MPaの圧力低下があったところで重合を停止したところ、1)と同様に無色透明のディスパージョンが得られた。

3) 2)に続いてSモノマー 50g、APS 0.1gを追加し、2)と同様の重合操作を2回繰り返し、16時間の後に重合を終了して無色透明のディスパージョン2160gを得た。

このディスパージョンは非常に安定で、塩酸やカリ明礬溶液などの電解質溶液を添加しても凝析しないので、そ

の一部から水分を蒸発させた後十分に乾燥し、これからアセトンで未反応のSモノマーを溶解回収して、物質収支によりポリマー得量とポリマー中のSモノマー含有量を算出すると、各々157g及び25.7モル%であった。

4) 3)のディスバージョン330gを純水で3倍に希釈し、APS 0.1gを添加し、1)~3)と同じ反応槽に仕込み、同様の操作で空間をHFPガスで置換後、0.45MPaに加圧し、さらにTFEガスで0.9MPaまで昇圧し、60°Cに昇温したところ直ちに圧力降下が始まった。4時間後に0.06MPaの圧力降下があったところで、20°Cに降温、放圧して重合反応を終了した。生成物は若干白濁した透明なディスバージョンであった。

【0032】このディスバージョンの一部を蒸発乾固し、アセトンで抽出してSモノマーを回収した結果から、ポリマー得量は81gであり、ポリマー中のSモノマー含有量は7.8モル%であった。本ポリマーはブロック共重合体と考えられる。得られたディスバージョンの¹⁹F-NMRを図1、視差熱重量分析(DTGA)の結果を図2に示す。ディスバージョンでも¹⁹F-NMRスペクトルが得られ、また官能基がSO₃Na型である本発明のポリマーの熱安定性が良好であることが明らかになった。

比較例1

HFPをコモノマーとして利用しない以外は、実施例1と同様にしてTFEとSモノマーの共重合体を得ることがで

*きる。得られる2元系共重合体は、生成ディスバージョンが不安定で長時間の重合反応により共重合体の凝析が起こりやすい。また、該2元系共重合体のディスバージョンは不安定であるため、限外濾過法や透析により精製する過程で共重合体の沈降が起こりやすく、限外濾過法や透析による未反応のSモノマーの除去、濃縮が困難である。

実施例2

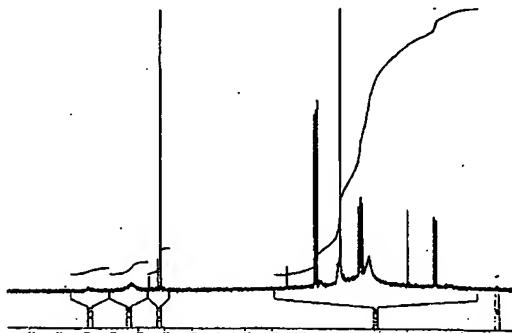
実施例1の1)~4)の各段階で生成するディスバージョンは極めて安定であるため限外濾過法の適用により未反応の残存Sモノマーを回収することができる。アミコン社のCentriprep(登録商標)のセルに実施例1の3)及び4)で生成したディスバージョンを入れ、室温1500Gの遠心分離条件下で処理すると、Sモノマーのみ限外濾過膜を透過する。更にディスバージョンをセルに追加して数回繰り返した後、次に純水を添加しながら同法を継続したところ、Sモノマーはほぼ完全に除去され、かつ、ポリマー濃度が60%の濃縮ディスバージョンを得ることができた。

20 【図面の簡単な説明】

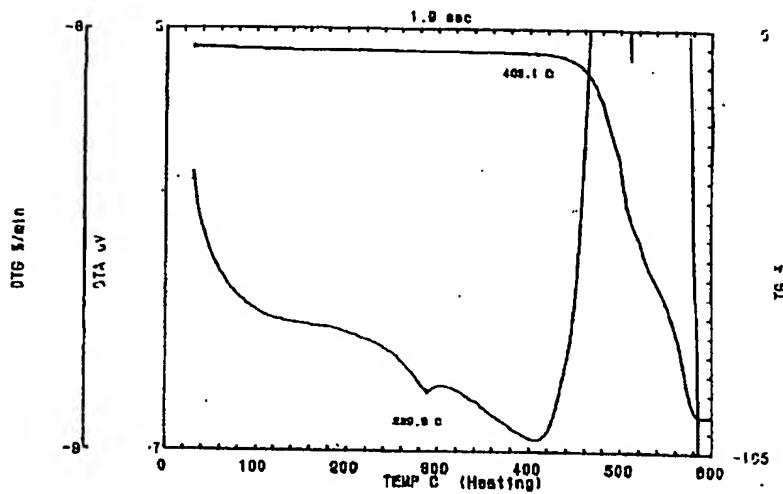
【図1】実施例1で得られたディスバージョンの¹⁹F-NMRを示す。

【図2】実施例1で得られたディスバージョンの視差熱重量分析(DTGA)の結果を示す。

【図1】



【図2】



フロントページの続き

F ターム(参考) 4J026 HA03 HA09 HA12 HA20 HA22
HA23 HA29 HA38 HB03 HB09
HB20 HB22 HB23 HB29 HE01
HE02
4J100 AA02R AC24R AC26Q AC27R
AC31R AE38P AE39R BA56P
BB07P CA04 CA05 GB12
JA16